

UNITED STATES ARMY

FRANKFORD ARSENAL

Engineering and Laboratory Evaluation to Improve Test
Procedures in Military Specification JAN-P-670,
Stabilized Red Phosphorus

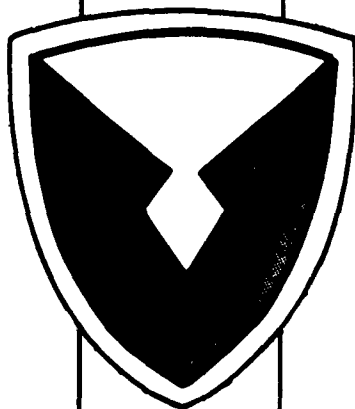
Test Report T63-8-1

March 1963

PHILADELPHIA 37, PA.

403-109

CAT. NO. 403-109
A. 10. 10.



Frankford Arsenal
Philadelphia 37, Pa.

Test Report T63-8-1
March 1963

Engineering and Laboratory Evaluation to Improve Test
Procedures in Military Specification JAN-P-670,
Stabilized Red Phosphorus

Prepared by: *George Norwitz*
GEORGE NORWITZ
Chemist

Joseph Cohen
JOSEPH COHEN
Chemist

Martin E. Everett
MARTIN E. EVERETT
Chemist

Reviewed by: *Samuel Sitekman*
SAMUEL SITEKMAN
Chief, Analytical Chemistry Section

R. D. France
R. D. FRANCE
Chief, Basic Materials Evaluation Br.

Approved by: *John J. Cummings*
JOHN J. CUMMINGS
Chief, Engineering Support Division

TABLE OF CONTENTS

	Page
I. INTRODUCTION	1
II. SUMMARY	2
III. RECOMMENDATIONS	2
IV. STUDY	
A. DETERMINATION OF COPPER	2
B. DETERMINATION OF IRON	4
C. DETERMINATION OF ALUMINUM	8
D. DETERMINATION OF TOTAL PHOSPHORUS	10
E. OKIDATION TEST	11
F. DETERMINATION OF YELLOW PHOSPHORUS AND GRANULATION	13
G. SPECIFICATION LIMITS	13
V. BIBLIOGRAPHY	14
VI. TABLES	16

I. INTRODUCTION

Red phosphorus is made by heating yellow phosphorus at 250° to 400° C. in the absence of air (9, 13). When intended for industrial use, it is ordinarily stabilized against oxidation by various means, usually by applying a coating of aluminum hydroxide by treating with aluminum sulfate and sodium hydroxide solutions (20). Another method for stabilization is to add a solution of sodium aluminate, and bubble air through the slurry at 85° to 95° C. for several hours (16). Mixing the red phosphorus with powdered aluminum or zinc provides some stability (20). Coating with phosphoric acid having a very low water content (21) and the addition of such compounds as mannitol, dextrose, and phloroglucinol (19) have been advocated.

Copper and iron increase the oxidation rate of red phosphorus significantly (20); therefore, rigid specification limits have been set for these elements (14). The removal of copper by treatment with alkaline sodium cyanide solution (15, 20) and the removal of iron by boiling with 5% sulfuric acid (20) have been proposed.

The present government specification for red phosphorus (14), which was established in 1948, recommends aluminum hydroxide as the stabilizing agent. It describes two procedures for the determination of aluminum (an aluminum phosphate method and an 8-hydroxyquinoline procedure) and two procedures for the determination of total phosphorus (the classical magnesium ammonium phosphate method and a colorimetric method). Methods for the determination of copper, iron, yellow phosphorus, oxidation rate, and granulation are also described.

II. SUMMARY

An improved colorimetric procedure for copper is proposed whereby the sample is dissolved in nitric acid and the solution evaporated to fumes of perchloric acid. Ammonium citrate, EDTA, and diethyldithiocarbamate are added, and the diethyldithiocarbamate complex is extracted with chloroform. An improved colorimetric procedure for iron is proposed whereby the sample is dissolved in nitric acid, the solution is evaporated to a small volume, and hydroxylamine hydrochloride, ortho-phenanthroline, and sodium citrate are added. It is recommended that the aluminum be determined by the 8-hydroxyquinoline procedure used by the National Bureau of Standards. The use of the classical magnesium ammonium phosphate method is recommended for the determination of total phosphorus. The oxidation test has been improved by use of an automatic recorder to measure the pressure and by use of a definite amount of water (0.5 ml) in the bomb. The methods previously proposed for yellow phosphorus and granulation are satisfactory.

III. RECOMMENDATIONS

It is recommended that the improved methods for copper, iron, aluminum, total phosphorus, and oxidation rate be incorporated into revised specification for red phosphorus.

IV. STUDY

A. DETERMINATION OF COPPER

The dithizone colorimetric method for copper in red phosphorus which is described in the specification (14) has been found to be unsatisfactory because of interferences and because three curves must be used for different concentrations. Copper in red phosphorus has also been determined colorimetrically by the use of diethyldithiocarbamate in ammonium citrate solution (2). This procedure is not entirely satisfactory since a colloidal suspension rather than a true solution is produced (17). Also, nickel, and cobalt interfere somewhat by contributing colors, and lead interferes by yielding a precipitate (2, 17).

In this report the extraction technique described by Claassen and Bastings (3, 17) is applied to the determination of copper in red phosphorus. In the method the diethyldithiocarbamate complex is extracted with chloroform from an ammonium citrate solution after adding

EDTA to complex iron, nickel, and cobalt. It has been pointed out (17) that phosphate can interfere when calcium is present, because of the precipitation of calcium phosphate which occludes some copper. No precipitation of aluminum phosphate was observed nor did phosphate interfere in any other way. The sample was dissolved in nitric acid and evaporated to fumes of perchloric acid as described in the present specification (14). No difficulty was observed from the slight attack of the beakers by the phosphoric acid, since detectable amounts of copper are not found in pyrex glass.

Reagents

Sodium diethyldithiocarbamate solution (0.1%). Dissolve 0.5 gram of sodium diethyldithiocarbamate in water and dilute to 500 ml. Store in an amber bottle.

Ammonium citrate solution (40%). Dissolve 200 grams of $(\text{NH}_4)_2\text{HC}_6\text{H}_5\text{O}_7$ in about 400 ml of water, make just ammoniacal to litmus paper with ammonium hydroxide (1 to 1), wash into a 500 ml separatory funnel, add 5 ml of diethyldithiocarbamate solution, and shake with 25 ml of chloroform for 1 minute. Drain and discard the chloroform layer, and dilute to 500 ml with water.

EDTA solution (5%). Dissolve 10 grams of EDTA in water and dilute to 200 ml.

Standard copper solution (1 ml = 0.01 mg of Cu). Dissolve 0.1964 gram of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in water, add 5 ml of hydrochloric acid, and dilute to 1 liter in a volumetric flask. Pipet a 50 ml aliquot into a 250 ml volumetric flask and dilute to the mark.

Preparation of Calibration Curve

Pipet 1.0, 2.0, 3.0, 4.0, and 5.0 ml of standard copper solution into 400 ml beakers, and add 25 ml of water and 2 ml of perchloric acid. Carry along a reagent blank. Add 5 ml of ammonium citrate solution (40%), 1 ml of EDTA solution (5%) and 2 drops of phenol red indicator. Add ammonium hydroxide until the solutions just changes to red, cool, and wash into 125 ml separatory funnels whose stems have been dried with wads of filter paper. Add 5 ml of sodium diethyldithiocarbamate solution (0.1%) and 10 ml of chloroform and shake for 1 minute. Drain the chloroform layers into dry 25 ml volumetric flasks, extract twice more with 5 ml portions of chloroform, and dilute to 25 ml with chloroform. Read the transmittance at 435 millimicrons with a spectrophotometer that has been set to 100% transmittance with the reagent blank. Plot mg of copper against % transmittance.

Procedure

Weigh a 1 gram sample into a 400 ml beaker, and add 10 ml of water and 35 ml of nitric acid. Carry along a reagent blank. Boil down to a volume of approximately 20 ml and add 2 ml of perchloric acid. Evaporate to fumes of perchloric acid, and fume for 1 to 2 minutes. Add 25 ml of water, 5 ml of ammonium citrate solution (40%), and 1 ml of EDTA solution (5%), and proceed as described in the preparation of the calibration curve. Convert the reading to mg of copper by referring to the calibration curve. Calculate as follows:

$$\% \text{ Cu} = \frac{\text{Mg of Cu}}{\text{grams of sample}} \times 10$$

(To calculate as p.p.m. multiply % by 10,000).

Results

The results obtained for iron in three samples of red phosphorus are shown in Table I. The first sample was red phosphorus that had been treated with alkaline sodium cyanide solution to reduce the copper content and with 5% sulfuric acid to reduce the iron content (20); the second sample was reagent grade red phosphorus (Mallinckrodt); the third sample was aluminated red phosphorus. Good recoveries were obtained when standard copper solution was added to the first sample and the synthetic mixtures were carried through the procedure (Table II).

B. DETERMINATION OF IRON

In the specification method for iron in red phosphorus, thiocyanate is added to the aqueous solution remaining after the dithizone extraction, and the iron complex is extracted with a mixture of amyl alcohol and ethyl ether (14). The method is of limited accuracy because of the strong repressive effect of phosphate on the thiocyanate color (17). The partial reduction of the ferric iron to the ferrous state by the dithizone is a source of difficulty since iron in the ferrous state does not give a color with thiocyanate. Another inaccuracy in the method is that it does not consider the attack on the beakers by the hot phosphoric acid (2). A method has been proposed by Brabson, Schaeffer, and Truchan (2) for the determination of iron

in red phosphorus by the use of ortho-phenanthroline (2) whereby the sample is dissolved in a mixture of 90 ml of carbon tetrachloride, 5 ml of bromine, 15 ml of nitric acid, and 75 ml of water, and the solution evaporated to a volume of 5 ml. Potassium chlorate is added to remove the yellow color and the solution is heated. The pyrophosphoric acid is then hydrolyzed by boiling with water, hydroxylamine hydrochloride, citric acid, and ortho-phenanthroline are added, and the pH is adjusted to 6 by adding ammonium hydroxide. It is necessary to establish a blank from an average of 6 runs by adding the reagents to phosphoric acid and proceeding as with the samples. The method is lengthy and cumbersome. Gassner (4) determined iron in condensed phosphate by boiling 30 minutes, adding citric acid, sodium sulfite, and hydroquinone. He then adjusted to a pH of 4, added 2,2'-bipyridine, and heated on a water bath for 3 hours. Grat-Cabanac (5) determined iron in phosphate by using sodium hyposulfite as the reducing agent, while Lohman, Kuemmel, and Sallee (11) extracted the iron with ether and then employed the usual ortho-phenanthroline method.

In this report an improved method is proposed for the determination of iron in red phosphorus by treating with nitric acid and evaporating to the appearance of nitrogen peroxide fumes at a volume of about 1 ml. This evolution of nitrogen peroxide takes place very suddenly and is preceded by foaming. The pyrophosphate is hydrolyzed by boiling with water, and hydroxylamine hydrochloride, ortho-phenanthroline, and a fairly large amount of sodium citrate are added. The sodium citrate buffers the solution at a pH of 5.5 and prevents the precipitation of aluminum phosphate. Bandemer and Schaible (1) used sodium citrate for the determination of iron in organic material. In their procedure, hydroquinone, ortho-phenanthroline, and sodium citrate (to obtain a pH of about 3.5) were added. The method is not applicable in the presence of large amounts of phosphate.

Reagents

Hydroxylamine hydrochloride solution (5%). Dissolve 25 grams of hydroxylamine hydrochloride in water and dilute to 500 ml.

Ortho-phenanthroline solution (0.2%). Dissolve 1 gram of ortho-phenanthroline in water and dilute to 500 ml. Store in a dark bottle.

Sodium citrate solution (20%). Dissolve 100 grams of $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 5\frac{1}{2} \text{H}_2\text{O}$ in water and dilute to 500 ml.

Standard iron solution (1 ml = 0.1 mg of Fe). Dissolve 0.1000 gram of pure iron (National Bureau of Standards Sample 55c) in 50 ml of hydrochloric acid by heating on the hot plate in an Erlenmeyer flask. Add 3 ml of hydrogen peroxide (30%), boil 10 minutes, cool, and dilute to 1 liter in a volumetric flask.

Preparation of Calibration Curve

Pipet 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 ml of standard iron solution into 100 ml volumetric flasks and add 35 ml of water. Carry along a reagent blank. Add 10 ml of hydroxylamine hydrochloride solution (5%) and allow to stand for 15 minutes. Add 10 ml of ortho-phenanthroline solution (0.2%) and 15 ml of sodium citrate solution (20%) and dilute to the mark. Allow to stand for 1 hour and read the transmittance at 510 millimicrons with a spectrophotometer that has been set to 100% transmittance with the reagent blank. Plot mg of iron against % transmittance.

Procedure

Clean 400 ml beakers (preferably unscratched) and pyrex watch glasses by rinsing with concentrated hydrochloric acid. Weigh a 0.5 gram sample and add 10 ml of water and 35 ml of nitric acid. Boil down on the hot plate at fairly high heat with the watch glass in place to the appearance of red nitrogen peroxide fumes at a volume of about 1 ml and immediately remove the beaker from the hot plate. Just prior to the appearance of the nitrogen peroxide the solution will start to foam. The beaker should be removed from the hot plate before the foaming has ceased. If the solution is heated too long (to the point at which white fumes appear) the determination should be discarded. Carry along a reagent blank prepared by adding 35 ml of nitric acid to 10 ml of water and evaporating just to dryness. After removing the beakers from the hot plate, allow to cool, add 75 ml of water, and boil down to approximately 35 ml with the watch glass in place. Cool to room temperature (but not lower), add 10 ml of hydroxylamine hydrochloride solution (5%), and allow to stand for 15 minutes. Add 10 ml of ortho-phenanthroline solution (0.2%) and 15 ml of sodium citrate solution (20%), dilute to 100 ml in a volumetric flask, and allow to stand for 1 hour. Read the transmittance at 510 millimicrons with a spectrophotometer that has been set at 100% transmittance with the reagent blank. Convert the reading to mg of iron by referring to the calibration curve. Calculate as follows:

$$\% \text{ Fe} = \frac{\text{Mg of Fe}}{\text{grams of sample} \times 10}$$

(To calculate as p.p.m. multiply % by 10,000).

Results

The results obtained for iron in the three samples previously used for the determination of copper are shown in Table I. Recoveries from synthetic samples are shown in Table III.

Discussion

It is recommended that the calibration curve be made up by the use of pure iron solution. The curve so obtained did not differ significantly from the curve obtained on adding standard iron solution to red phosphorus and carrying the samples through the procedure.

The blank for the method was obtained by evaporating the nitric acid to dryness. The addition of phosphoric acid to the blank as suggested by some investigators (2) is undesirable, since it is difficult to judge what the iron content of the phosphoric acid is and how much phosphoric acid should be present.

All beakers and watch glasses must be rinsed with hydrochloric acid to remove any iron. It is a wise policy to reserve special beakers and watch glasses for the determination of iron. No detectable amounts of iron are dissolved from the beakers, if the beakers are removed from the hot plate when the red nitrogen peroxide fumes appear. The evolution of the nitrogen peroxide is probably caused by the reduction of the last traces of nitric acid by the lower acids of phosphorus. Evidence that the beakers are not appreciably attacked are the results obtained for the high purity sample containing 0.001% iron (Table I). The reproducibility of the method is further evidence, since such an attack would cause erratic results. If the heating on the hot plate is prolonged beyond the appearance of the nitrogen peroxide (to the appearance of white fumes of phosphoric acid) then the glass will be attacked and somewhat higher results will be obtained. The iron content of pyrex glass is about 0.1% (18). Experiments were conducted with the use of platinum dishes instead of pyrex beakers, but erratic results were obtained from the iron present in platinum (7). The platinum itself did not seem to be attacked.

The maximum amount of red phosphorus that can be handled in the method is 0.5 gram.

A large excess of hydroxylamine hydrochloride and ortho-phenanthroline is necessary to obtain full color development.

The boiling is necessary to convert the pyrophosphates to phosphates. The interference from the former is greater than the latter (17).

C. DETERMINATION OF ALUMINUM

As stated previously, both the aluminum phosphate and 8-hydroxyquinoline methods are recommended in the specification (14). The aluminum phosphate method was found to be unreliable in the hands of several operators in this laboratory. Frequently, low results were obtained probably because of the formation of soluble aluminum complexes with the excess of phosphate present. Another difficulty with the method is that the aluminum phosphate precipitate is not stoichiometric (7). In view of the limitations of the method, it is recommended that it be abandoned. The 8-hydroxyquinoline method described in the specification (14), whereby the sample is dissolved in nitric acid, the solution evaporated to fumes of perchloric acid, and the aluminum 8-hydroxyquinolate precipitated from an ammoniacal solution, gave reproduceable results. However, it is recommended that the technique used by the National Bureau of Standards (7) be employed. That agency recommended a different preparation of the reagent solution and wash solution and drying at 135° C. in convection oven (instead of a vacuum oven).

The amount of aluminum picked up by the slight attack on the beakers by the phosphoric acid did not cause any significant error. This was checked by evaporating a mixture of 5 ml of perchloric acid and 1 ml of phosphoric acid to fumes and proceeding as in the method. No precipitate was obtained.

The method is recommended for the analysis of aluminated red phosphorus containing approximately 2 to 3% aluminum hydroxide.

It is suggested that a microscopic examination of the red phosphorus be made to ensure that the aluminum is not present as aluminum metal. In some instances, producers have mixed the red phosphorus with powdered aluminum metal instead of coating it with aluminum hydroxide.

Reagents

8-Hydroxyquinoline solution (2.5%). Dissolve 12.5 grams of 8-hydroxyquinoline in 25 ml of glacial acetic acid by warming gently on the hot plate. Dilute to 500 ml with water. Filter just before using if not clear.

Wash solution. Add 12 ml of 8-hydroxyquinoline solution to about 500 ml of water, add 30 ml of ammonium hydroxide (1 to 1), and dilute to 500 ml. Prepare just before using.

Procedure

Weight a 1 gram sample into a covered 400 ml beaker and add 10 ml of water and 35 ml of nitric acid. Boil down to a volume of approximately 20 ml and add 5 ml of perchloric acid. Evaporate to strong fumes of perchloric acid and fume for 1 minute. Add about 50 ml of water and if the solution is not clear, filter, and wash with water. Dilute to approximately 200 ml with water and add 10 ml of 8-hydroxyquinoline solution (2.5%). Make just alkaline to litmus paper with ammonium hydroxide (1 to 1) and add 20 ml of ammonium hydroxide (1 to 1) in excess. Wash down and remove the litmus paper. Heat to 60° to 70° C. (use a thermometer) and digest at this temperature for 30 minutes. Cool to about 15° C. in a cold water bath and filter through a tared sintered glass crucible of medium porosity. Transfer the precipitate to the crucible and wash four times with the wash solution. Finally, wash the precipitate twice with cold water. Dry at 135° C. for 90 minutes, cool, and weigh. Calculate as follows:

$$\% \text{ Al(OH)}_3 = \frac{16.98 \times \text{grams of precipitate}}{\text{grams of sample}}$$

Results

The results obtained for aluminum in a sample of aluminated red phosphorus are shown in Table IV. The recoveries obtained on adding standard aluminum solution to reagent grade phosphorus are shown in Table V. A correction was made for the small amount of aluminum this sample contained (about 0.1%).

D. DETERMINATION OF TOTAL PHOSPHORUS

As stated previously, the classical magnesium ammonium phosphate method and a colorimetric method have been recommended for the determination of total phosphorus (14). The colorimetric method which was a modification of a method used previously for the determination of up to 0.8% phosphorus in iron and steel (6) is not sufficiently accurate for the determination of phosphorus in red phosphorus and should be abandoned. It is suggested that the phosphorus be determined by the classical magnesium ammonium phosphate method (7, 14). Essentially the method to be described in the present report is the one used in the specification. The sample is dissolved in nitric acid, the solution is evaporated to strong fumes of perchloric acid to oxidize the phosphorus to the pentavalent state, and a double precipitation of the magnesium ammonium phosphate is made in the presence of ammonium citrate. The factor for converting $\text{Mg}_2\text{P}_2\text{O}_7$ to phosphorus on the basis of the latest atomic weights is 0.2783 (8) rather than 0.2786 used in the specification.

Reagents

Magnesia mixture. Dissolve 50 grams of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and 100 grams of ammonium chloride in about 500 ml of water, add ammonium hydroxide in slight excess, allow to stand overnight, and filter if a precipitate appears. Make just acid with hydrochloric acid and dilute to 1 liter.

Ammonium citrate solution (20%). Dissolve 200 grams of $(\text{NH}_4)_2\text{HC}_6\text{H}_5\text{O}_7$ in water and dilute to 1 liter.

Procedure

Transfer a 1 gram sample to a 400 ml beaker and add 10 ml of water and 35 ml of nitric acid. Cover with a watch glass, warm on the hot plate until the vigorous reaction ceases, and then boil down to a volume of approximately 20 ml. Add 10 ml of perchloric acid and boil down to a volume of 3 or 4 ml. Cool, add water, and dilute to 500 ml in a volumetric flask. Pipet a 25 ml aliquot (equivalent to 0.05 gram of sample) into the original beaker, and add 50 ml of water, 15 ml of ammonium citrate solution (20%), and 150 ml of magnesia mixture. Add ammonium hydroxide (1 to 1) with stirring until the precipitate starts to appear, stop the addition of the ammonium hydroxide, and stir for about 2 minutes. Add 25 ml of ammonium hydroxide (1 to 1) in excess and allow to stand overnight. Filter through a Whatman No. 40 filter paper, wash the precipitate into the filter paper with ammonium hydroxide (1 to 50), and then wash three times with ammonium hydroxide (1 to 50). Dissolve the

precipitate off the filter paper into the original 400 ml beaker with two 12 ml portions of hydrochloric acid (1 to 1) and then wash several times with hot hydrochloric acid (1 to 50). Add 1 ml of ammonium citrate solution and 4 ml of magnesia mixture and again precipitate by adding ammonium hydroxide as previously described. Add 10 ml excess ammonium hydroxide (1 to 1) and allow to stand overnight. Filter through a Whatman No. 40 filter paper, transfer the precipitate to the filter paper with ammonium hydroxide (1 to 50), and wash five times with ammonium hydroxide (1 to 50). Transfer the filter paper and precipitate to a tared porcelain crucible, and char and burn off the filter paper at low heat. Ignite over a Meker burner until the precipitate is white, then ignite over a blast burner for 15 minutes. Cool and weigh as $Mg_2P_2O_7$. Calculate as follows:

$$\% P = \frac{27.83 \times \text{grams of precipitate}}{\text{grams of sample}}$$

Results

The results obtained for phosphorus in samples of reagent grade phosphorus and aluminated red phosphorus are shown in Table VI. The precision was excellent. It is not feasible to check a method of this type for accuracy by using the addition technique.

E. OXIDATION TEST

It has been known for a long time that the presence of moisture affects the oxidation rate of red phosphorus (12). For this reason in the oxidation test for red phosphorus (14) moistened glass wool is placed in the bomb. The amount of water is not specified. According to experiments in this laboratory, increasing the amount of water (from 0.1 ml upwards) does not change the length of the induction period significantly; however, the slope of the oxidation curve following the induction period is greater. It is recommended, therefore, that a definite amount of water be added.

In the specification (14) the pressures are read from a dial at stated intervals. This laboratory has installed an automatic recorder to make a continuous record of the bomb pressures. It is suggested that the revised specification adopt the automatic recording method as the preferred method, and the visual reading method as an alternate method.

The induction time of 20 hours minimum should be retained for both the visual and automatic recording methods. It is recommended that the maximum oxidation rate of 1.6 p.s.i. decrease in pressure per hour be retained for the visual method but that the limit be changed to 1.4 p.s.i. for the automatic recording method. The reason for this difference is that the volume of oxygen in the automatic recording method is greater because of the oxygen contained in the tubing connecting the bomb to the automatic recorder. It is obviously necessary to fix the volume of the tubing and this is done by using the tubing specified.

Apparatus

Norma-Hoffman oxygen bomb (Precision Scientific Co., 73414, Catalogue No. 40; Fisher Scientific Co., 13-555-200, Catalogue 59).

Recording pressure gauge (Fisher Scientific Co., 13-555-130, or 13-555-135, or 13-555-140, Catalogue 59).

Copper or bronze tubing for connecting the bomb to the automatic recorder (this tubing is not needed if the readings are made visually). The tubing is 3/16 inch in internal diameter, and 9 feet long (total length). It contains a helix (5 turns, 2-1/2 inches in diameter) to provide flexibility. It has couplings at its ends and a valve a few inches from the recorder to bleed off the oxygen.

Special 50 ml beaker. Eliminate the lip and protruding rim of a 50 ml beaker by shaping in a flame. This treatment is necessary to permit the beaker to fit into the bomb.

Procedure

Place a flat wad of pyrex wool (0.1 to 0.2 gram) into the bottom of the bomb and add 0.5 ml of water measured with a pipet. Weigh a 5 gram sample into the special 50 ml beaker and cover with a watch glass. Place the beaker on top of the glass wool. Bolt the bomb securely and flush with oxygen, bringing the bomb pressure up to 50 p.s.i. and releasing three times. Allow 45 to 50 p.s.i. pressure to remain and place the bomb in a bath maintained at 110° C. Release the pressure intermittently to exactly 50 p.s.i. until there is no further increase.

Record the pressure using the automatic recorder. An alternate (but less desirable) procedure is to make the readings visually at 1/2 hour intervals for 1-1/2 hours and at 2 hour intervals thereafter.

Plot cumulative pressure drop against time (see Figure 2 of the specification (14)), considering the zero time to be 3/4 hour after the bomb is placed in the bath. The curve is characterized by a portion of moderate slope containing a linear portion, followed by a portion of greater slope which also contains a linear portion and which tapers off. The induction period is defined as the abscissa (AE') of the intersection of the two linear portions extended (BB' and MM'). The oxidation rate is defined as the slope of the second linear portion (MM') (see paragraph H-3 of the specification (14)).

F. DETERMINATION OF YELLOW PHOSPHORUS AND GRANULATION

The tests for yellow phosphorus (10, 14) and granulation (14) described in the specification are satisfactory.

G. SPECIFICATION LIMITS

The specification limits in the specification (14) are satisfactory with the exception of the oxidation rate for the automatic recording method mentioned in the study of the oxidation test.

V. BIBLIOGRAPHY

- (1) Bandemer, S. L., and Schaible, P. J., Ind. Eng. Chem., Anal. Ed., 16, 317 (1944).
- (2) Brabson, J. A., Schaeffer, P. A., Truchan, A., and Deal, L., Ind. Eng. Chem., Anal. Ed., 18, 554 (1946).
- (3) Claassen, A., and Bastings, L., Z. anal. Chem., 153, 30 (1956).
- (4) Gassner, K., Z. anal. Chem., 153, 81 (1956).
- (5) Grat-Cabanac, M., Anal. Chim. Acta, 5, 116 (1951).
- (6) Hague, J. L., and Bright, H. A., J. Research Natl. Bur. of Standards, 26, 405 (1941).
- (7) Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., "Applied Inorganic Analysis", pp. 21, 505, 508, 704, John Wiley, New York, 1953.
- (8) Hodgman, C. D., "Handbook of Chemistry and Physics", p. 1683, Chemical Rubber Publishing Co., Cleveland, Ohio, 1956.
- (9) Kirk, R. E., and Othmer, D. F., "Encyclopedia of Chemical Technology", Vol. 10, p. 452, Interscience Publishers, New York, 1953.
- (10) Kray, R. H., Ind. Eng. Chem., 19, 816 (1927).
- (11) Lohman, F. H. Kuenkel, D. F., and Saltee, E. M., Anal. Chem., 31, 1739 (1959).
- (12) Mellor, J. W., "Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. 8, p. 773, Longmans, Green, and Co., London, 1931.
- (13) Miller, P., Wilson, R. A., and Tusson, J. R., Ind. Eng. Chem., 40, 357 (1948).
- (14) National Military Establishment Specification, Stabilized Red Phosphorus, JAN-P-670 (1948).
- (15) Nordblom, G. F., U. S. Patent 2,636,811 (1953).

- (16) Pernert, J. C., U. S. Patent 2,359,243 (1944).
- (17) Sandell, E. B., "Colorimetric Determination of Traces of Metals", pp. 169, 444, 530, 540, Interscience Publishers, New York, 1959.
- (18) Scholes, S. R., "Modern Glass Practice", p. 46, Industrial Publications, Chicago, 1941.
- (19) Silverstein, M. S., U. S. Patent 2,440,303 (1948).
- (20) Silverstein, M. S., Nordblom, G. F., Dittrich, C. W., and Jakabcin, J. J., Ind. Eng. Chem., 40, 301 (1948).
- (21) Skolnik, S., and Bridger, G. L., U. S. Patent, 2,559,684 (1951).

VI. TABLES

Table I. Results for Copper and Iron in Samples of Red Phosphorus

<u>Sample</u>	<u>Cu Found (%)</u>	<u>Fe Found (%)</u>
p ^a	0.0003	0.001
	0.0004	0.001
	0.0003	0.001
	0.0004	0.001
	0.0004	0.001
	Avg. 0.0004	0.001
	Std. Dev. 0.00007	0.000
m ^b	0.0009	0.0178
	0.0009	0.0150
	0.0006	0.0168
	0.0008	0.0170
	0.0009	0.0170
	Avg. 0.0008	0.0167
	Std. Dev. 0.00013	0.0010
A ^c	0.0006	0.004
	0.0004	0.004
	0.0004	0.003
	0.0005	0.003
	0.0006	0.004
	Avg. 0.0005	0.004
	Std. Dev. 0.00010	0.0007

^a Specially purified

^b Reagent grade red phosphorus

^c Aluminated red phosphorus

Table II. Recovery of Copper Added to Synthetic Samples

<u>Synthetic Sample</u>	<u>Total Cu Present (mg)</u>	<u>Total Cu Found (mg)</u>	<u>Cu Recovered (mg)</u>
1 g P ^a + 0.005 mg Cu	0.009	0.008	0.004
1 g P + 0.01 mg Cu	0.014	0.013	0.009
1 g P + 0.03 mg Cu	0.034	0.030	0.026
1 g P + 0.04 mg Cu	0.044	0.043	0.039
1 g P + 0.05 mg Cu	0.054	0.051	0.047

^a Contains 0.0004% Cu (Table I)

Table III. Recovery of Iron Added to Synthetic Samples

<u>Synthetic Sample</u>	<u>Total Fe Present (mg)</u>	<u>Total Fe Found (mg)</u>	<u>Fe Recovered (mg)</u>
0.5 g P ^a + 0.02 mg Fe	0.025	0.030	0.025
0.5 g P + 0.05 mg Fe	0.055	0.054	0.049
0.5 g P + 0.10 mg Fe	0.105	0.105	0.100
0.5 g P + 0.20 mg Fe	0.205	0.202	0.197
0.5 g P + 0.30 mg Fe	0.305	0.296	0.291

^a Contains 0.001% Fe (Table I)

Table IV. Results for Aluminum in a Sample of Aluminated Red Phosphorus

	<u>% Al (OH)₃ Found</u>
	2.92
	2.92
	2.95
	2.92
	2.95
Avg.	2.93
Std. Dev.	0.017

Table V. Recovery of Aluminum Added to Synthetic Samples

<u>Synthetic Sample</u>	<u>Aluminum Recovered (mg) ^{a, b}</u>
1 g M + 5.0 mg Al	5.14
1 g M + 10.0 mg Al	9.95
1 g M + 15.0 mg Al	15.21
1 g M + 20.0 mg Al	19.96

^a The factor for converting aluminum 8-hydroxyquinolate to aluminum is 0.0587

^bDeduction made for the small amount of aluminum present in M

Table VI. Results for Total Phosphorus in Samples of Red Phosphorus

<u>Sample</u>	<u>Phosphorus Found (%)</u>
M ^a	95.32
	95.21
	95.21
	95.10
	Avg. 95.21
	Std. Dev. 0.090
A ^b	93.49
	93.65
	93.43
	93.54
	Avg. 93.53
	Std. Dev. 0.093

^a Reagent grade red phosphorus

^b Aluminated red phosphorus

DISTRIBUTION LIST

- 2 - Commanding General
U. S. Army Missile Command
Redstone Arsenal, Alabama
ATTN: B. J. Alley, AMSMI-RKC
W. W. Howard, AMSMI-RKC
- 2 - Rocket Propulsion Laboratories
Edwards, California
ATTN: W. S. Anderson, DGPC
H. E. Malone
- 3 - Commanding Officer
Naval Ordnance Test Station
China Lake, California
ATTN: E. M. Bens
W. H. Rice
Technical Library Branch
- 4 - Commanding Officer
U. S. Naval Propellant Plant
Indian Head, Maryland
ATTN: M. Fauth
H. L. Stalcup, Q5A
Technical Library
J. Tuono
- 1 - Director
Naval Research Laboratory
Washington 25, D. C.
ATTN: R. N. Hazlett
Code 6180
- 3 - Commanding Officer
Picatinny Arsenal
Dover, New Jersey
ATTN: M. Roth
A. Sokol, SMUPA-DC-7
S. Wachtell
- 1 - National Aeronautics and Space
Administration
Lewis Research Center
21000 Brookpark Road
Cleveland 35, Ohio
- 1 - Army Missile Command
Research Laboratory, OMLD
Huntsville, Alabama
ATTN: W. W. Wharton
Code AMSMI-ORC
- 1 - Rohm and Haas Company
Redstone Arsenal Research Division
Huntsville, Alabama
ATTN: K. A. Booman
- 1 - Space Technology Laboratories
1 Space Park
Redondo Beach, California
ATTN: Dr. E. A. Burns
- 1 - Sandia Corporation
Sandia Base
P. O. Box 5800
Albuquerque, New Mexico
ATTN: R. J. Buxton
- 1 - Rocketdyne
6633 Canoga Avenue
Canoga Park, California
ATTN: E. F. C. Cain
- 1 - Thiokol Chemical Corporation
Redstone Division
Huntsville, Alabama
ATTN: J. R. Denson
- 1 - Aerojet-General Corporation
P. O. Box 1947
Sacramento, California
ATTN: T. P. Harrington
- 1 - Jet Propulsion Laboratory
4800 Oak Grove Drive
Pasadena 3, California
ATTN: A. J. Havlik
- 1 - Reaction Motors Division
Thiokol Chemical Corporation
Denville, New Jersey
ATTN: F. G. Hoffman
- 2 - United Technology Corporation
1050 E. Arques Avenue
Sunnyvale, California
ATTN: H. J. Hyer
P. O. Marti

- 1 - Thiokol Chemical Corporation
Elkton Division
Elkton, Maryland
ATTN: R. M. Jones
- 3 - Aerojet-General Corporation
P. O. Box 296
Azusa, California
ATTN: W. H. Kaelin
J. L. Myers
E. M. Wilson
- 3 - The Chemical Propulsion Information
Agency
The Johns Hopkins University
Applied Physics Laboratory
8621 Georgia Avenue
Silver Spring, Maryland
ATTN: S. S. Miller
- 1 - Stanford Research Institute
Menlo Park, California
ATTN: R. F. Muraca
- 1 - Thiokol Chemical Corporation
Marshall, Texas
ATTN: J. H. Murphey, Jr.
- 1 - Rocketdyne, A. Division of North
American Aviation, Inc.
Solid Propulsion Operations
P. O. Box 548
McGregor, Texas
ATTN: C. R. Neff
- 1 - E. I. duPont deNemours
Penns Grove, New Jersey
ATTN: J. R. Ness
- 1 - Hercules Powder Company
Kenvil, New Jersey
ATTN: H. A. Read
- 1 - Commanding Officer
Hercules Powder Company
Radford Arsenal
Radford, Virginia
ATTN: E. G. Simpson
- 1 - Hercules Powder Company
Allegany Ballistics Laboratory
P. O. Box 210
Cumberland, Maryland
ATTN: A. W. Tiedemann, Jr.
- 1 - Allied Chemical Corporation
General Chemical Division
Research Laboratory
P. O. Box 405
Morristown, New Jersey
ATTN: A. D. Turissini
- 1 - Callery Chemical Company
Research and Development
Callery, Pennsylvania
ATTN: A. E. Weber
- 1 - Minnesota Mining and Manufacturing
Company
900 Bush Avenue
St. Paul 6, Minnesota
ATTN: D. G. Weiblen
- 2 - Commanding General
Aberdeen Proving Ground
Maryland
ATTN: Ballistic Research
Laboratories STEAP-BLI
G. L. D'Angelis
- 2 - Headquarters
Ogden Air Material Area
Hill Air Force Base, Utah
ATTN: N. M. Hansen
N. W. Harbertson, OOOEE
- 1 - Commanding Officer
Longhorn Ordnance Works
Marshall, Texas
ATTN: M. R. Kesling
- 1 - Canadian Armament Research and
Development Establishment
Quebec, Canada
ATTN: R. MacDonald

1 - Canadian Arsenals, Ltd. Quebec, Canada ATTN: W. L. Phene	1 - Scientific and Tech. Info. Facility P. O. Box 5700 Bethesda, Maryland ATTN: NASA Representative
1 - Chemical Inspectorate Renfrewshire, Scotland ATTN: C. M. Robertson	1 - Air Proving Ground Center Eglin Air Force Base Florida ATTN: PGAPI
1 - Commander Naval Ordnance Laboratory White Oak, Silver Spring, Maryland ATTN: J. M. Rosen	10 - Armed Services Tech. Info. Agency Arlington Hall Station Arlington 12, Virginia ATTN: TIPCR
1 - Headquarters U. S. Army CBR Quality Assurance Group Edgewood Arsenal, Maryland ATTN: T. Sinclitico	1 - Commanding General Ammunition Procurement & Supply Agcy Joliet, Illinois ATTN: APSLY-AREL, Engr. Library
1 - U. S. Department of the Interior Bureau of Mines 4800 Forbes Avenue Pittsburgh 13, Pennsylvania ATTN: M. M. Dolinar, Reports Librarian, Explosive Research Laboratory	1 - Bermite Powder Company Saugus, California
1 - Nat'l Aeronautics & Space Administration Washington 25, D. C. ATTN: Office of Technical Info & Educational Programs, Code ETL	
28 - U. S. Army Ammunitions Command FRANKFORD ARSENAL Philadelphia 37, Pa. ATTN: Thru; Chief, 1000 Atg. Chief, 1000 Inst for Research, 1010 Assoc Dir for ES-S, 1100 Chief, 1700 L. H. Adam, 1700 Chief, 1720 Chief, 1721 Chief, 1723 G. Norwitz, 1723 J. Cohen, 1723 M. E. Everett, 1723 M. A. Fry, 5500 J. Charno, 6152 Chief, 1214	(1) (1) (1) (1) (1) (1) (1) (5) (3) (2) (2) (2) (2) (3) (2) (3)